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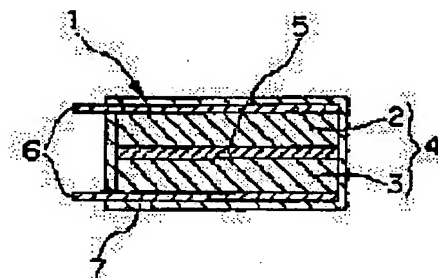
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(54) ENTIRE SOLID LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To eliminate occurrence of leak of an electrolyte, improve safety, and improve a charge/discharge cycle characteristic by impregnating solid electrolyte and electrodes with a polymeric solid electrolyte containing solute and polymerizing them.

SOLUTION: Polymeric solid electrolyte containing solute is impregnated into a pair of electrodes 4 comprising solid electrolyte 5 using lithium oxide containing transition metal such as Ti, V, Cr, Mn, Fe, Co, or Ni, a positive electrode 2, and a negative electrode 3, and they are polymerized. This polymeric solid electrolyte is composed of one or plural kinds of polyethylene-oxide polymeric solid electrolyte and polypropylene-oxide polymeric solid electrolyte, and the solute is composed of one or plural kinds of LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiC}(\text{CF}_3\text{SO}_2)_2$. Thus, a contact area of the solid electrolyte 5 and the electrodes 4 can be increased, therefore, movement of lithium ions following a charge/ discharge reaction is smoothened, and internal resistance of this secondary battery can be reduced.



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CLAIMS

[Claim(s)]

[Claim 1] All the solid-state lithium secondary batteries characterized by having infiltrated the aforementioned solid electrolyte and the solid polymer electrolyte which contains a solute in an electrode in all the solid-state lithium secondary batteries formed combining the material which shows a solid electrolyte, the occlusion of the ion accompanying an electrochemical oxidation-reduction reaction for an electrode, and a discharge phenomenon, and carrying out a polymerization.

[Claim 2] The aforementioned solid polymer electrolyte consists of any one sort of a polyethylene-oxide system solid polymer electrolyte or the polypropylene oxide system solid polymer electrolyte, or two or more sorts, and the aforementioned solute is LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiC}(\text{CF}_3\text{SO}_2)_2$. All solid-state lithium secondary batteries according to claim 1 characterized by consisting of any one sort or two or more sorts.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to all the solid-state lithium secondary batteries that used the solid-state-like electrolyte as an electrolyte.

[0002]

[Description of the Prior Art] Although the various cells which used the electrolyte of a drainage system or a non-drainage system for inter-electrode [of a positive/negative couple] were developed from the former, it was not what should be satisfied in respect of the rate property in charge and discharge, a cycle property, a preservation property, or an energy density with the thin shape of video photography equipment in recent years, a notebook computer, or a portable information terminal equipment like a cellular phone, and a lightweight miniaturization.

[0003] As a cell with which are satisfied of such many properties, the research and development of a rechargeable battery which have a high energy density are briskly done by the high voltage, and the lithium secondary battery which used the metal lithium for the negative electrode is in the limelight as an object for the power supplies of a portable information **** device as a lightweight and reusable small rechargeable battery especially.

[0004] However, although this metal lithium was rich in reactivity, since the conventional lithium secondary battery used the metal lithium for the negative electrode, and there was a possibility of igniting suddenly with the material which is easy to burn, there was an essential problem in respect of security.

[0005] In order to solve such a problem, the lithium secondary battery which transposed the negative electrode to the material which has the layer structure of a graphite etc. as a material which constitutes an electrode is proposed (refer to JP,7-12226,A).

[0006] However, since this lithium secondary battery is using as the negative electrode the graphite which has the layer structure, Various end groups, such as a quinone machine combined with this graphite front face and a ketone group, have many which are easy to be returned electrochemically. In the 1st initial charge reaction, gas occurs by the electrochemical-reduction reaction related to the end group and the electrolyte, and the internal pressure of a cell rises. Since the cell exploded, degradation of a cell performance arose and also the inflammable organic system electrolytic solution which dissolved lithium salt in the electrolyte was used, there was a problem of a liquid spill and there was a problem that the edfety of double Mie was required, too for safety reservation.

[0007] Moreover, the solid electrolyte which consists of an organic macromolecule and the organic system electrolytic solution is made to intervene between the positive/negative poles of a couple, and the lithium secondary battery which pressed down the electrolytic fluidity is also proposed (JP,8-315855,A).

[0008] However, this lithium secondary battery contains the organic system electrolytic solution, and in the charge-and-discharge process at the time of an elevated temperature, this organic system electrolytic solution starts a decomposition reaction, it generates gas, and there is a problem that the internal pressure of a cell rises.

[0009]

[Objects of the Invention] this invention aims at offering all the solid-state lithium secondary batteries whose cycle properties of charge and discharge accomplished in view of the technical problem of such conventional technology, the electrolyte generated gas in the oxidation-reduction reaction, and exploded, or canceled that an electrolytic liquid spill etc. occurred, and were excellent in safety, and improved.

[0010]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, according to all the solid-state lithium secondary batteries concerning this invention, in all the solid-state lithium secondary batteries formed combining the material which shows a solid electrolyte, the occlusion of the ion accompanying an electrochemical oxidation-reduction reaction for an electrode, and a discharge phenomenon, the aforementioned solid electrolyte and the solid polymer electrolyte which contains a solute in an electrode were infiltrated, and the polymerization was carried out.

[0011] Moreover, in all the above-mentioned solid-state lithium secondary batteries, the aforementioned solid polymer electrolyte consists of any one sort of a polyethylene-oxide system solid polymer electrolyte or the polypropylene oxide system solid polymer electrolyte, or two or more sorts, and the aforementioned solute is LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiC}(\text{CF}_3\text{SO}_2)_2$. It is desirable to consist of any one sort or two or more sorts.

[0012]

[Function] In all the solid-state lithium secondary batteries of this invention, from not using a liquid, especially the organic system electrolytic solution for the electrolyte An electrolytic liquid spill is lost and an electrolyte does not cause moisture, air, and a reaction further. moreover, from infiltrating a solid electrolyte and the solid polymer electrolyte which contains a solute in an electrode, and carrying out a polymerization In elegance, a solid polymer electrolyte will exist in the opening of the solid electrolyte particle in the state near a point contact, and an electrode active material particle conventionally. The touch area of a solid electrolyte and an electrode can be made to increase, movement of the lithium ion accompanying a charge-and-discharge reaction becomes smooth, and it can consider as all the solid-state lithium secondary batteries that are excellent in a rechargeable battery property.

[0013]

[Embodiments of the Invention] Hereafter, the operation gestalt of all the solid-state lithium secondary batteries of this invention is explained in detail based on an accompanying drawing. Drawing 1 is the cross section showing 1 operation gestalt of all the solid-state lithium secondary batteries of this invention. In drawing 1, 1 is all solid-state lithium secondary batteries that consist of a positive electrode 2, the electrode 4 of the couple which consists of a negative electrode 3, and a solid electrolyte 5, the positive electrode 2 and negative electrode 3 which accomplish the electrode 4 of a couple are applied to a charge collector 6, are formed, make a solid electrolyte 5 intervene between the electrodes 4 of a couple, and sheathing of them is carried out and they consist of packages 7 which can hold airtightness.

[0014] All the solid-state lithium secondary batteries of this invention show the occlusion and the discharge phenomenon of ion accompanying an electrochemical oxidation-reduction reaction, and an electrode 4 and a solid electrolyte 5 consist of combination of the material which has the charge and discharge potential mentioned later, this phenomenon is shown, and especially if it has predetermined charge and discharge potential, they will not limit them. For example, LiCoO_2 , LiNiO_2 , LiCrO_2 , and LiVO_2 , $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_4$, LiMn_2O_4 , and LiMnO_2 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$, LiTiO_2 , LiFeO_2 , LiRuO_2 , LiWO_2 , $\lambda\text{-MnO}_2$, V_2O_5 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, anatase type TiO_2 , and Nb_2O_5 etc. — a well-known material can be used

[0015] If the electromotive force of a rechargeable battery is taken into consideration, it is more suitable that it is desirable for the difference of the charge and discharge potential of the material which constitutes an electrode 4 to be size, and the charge and discharge potential of the material which constitutes a solid electrolyte 5 is still lower than they. For example, the active material which constitutes an electrode 4 consists of the material whose charge and discharge potential of a positive electrode 2 is 2.5–4.0V by making a metal lithium into a reference potential, and it consists of the material whose charge and discharge potential of a

negative electrode 3 is 2.0–3.0V, and, as for a solid electrolyte 5, it is more desirable to consist of the material the charge and discharge potential of whose is 1.5–2.9V by making a metal lithium into a reference potential.

[0016] A metal lithium is made into a reference potential, the charge and discharge potential makes low material the material of a solid electrolyte 5 most, the material which shows middle charge and discharge potential is applied to the active material material which constitutes a negative electrode 3, the material which shows the highest charge and discharge potential is combined as an active material material which constitutes a positive electrode 2, by making a metal lithium into a reference potential, that the difference of the charge and discharge potential of a positive electrode 2 and a negative electrode 3 is large can obtain higher charge and discharge potential, and it serves as a desirable combination. That is, the charge and discharge potential of all the solid-state lithium secondary batteries of this invention is because it is determined by the difference of the charge and discharge potential of a positive electrode 2 and a negative electrode 3 like other rechargeable batteries.

[0017] It is LiCoO_2 the charge and discharge potential specifically indicates about 4 V to be by making a metal lithium into a reference potential. If it chooses as an active material material which constitutes a positive electrode 2 LiMnO_2 charge and discharge potential indicates about 3 V to be to the active material material which constitutes a negative electrode 3 It can choose. It is desirable to use for the material of a solid electrolyte 5 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which shows the charge and discharge potential of about 1.55 V, for example from it being more nearly required than the charge and discharge potential of the active material material which constitutes a negative electrode 3 to be what has low charge and discharge potential further. If a layered product is formed as a positive electrode 2, a negative electrode 3, and a solid electrolyte 5, respectively and the charge and discharge potential is measured with this combination, it can check that the charge and discharge potential of about 1 V is shown.

[0018] moreover, as an example which uses a metallic oxide for a negative electrode 3 Anatase type TiO_2 the charge and discharge potential indicates about 1.8 V to be to the active material material which constitutes a negative electrode 3 by making a metal lithium into a reference potential It can choose. LiMn_2O_4 charge and discharge potential indicates about 4 V to be to the active material material which constitutes a positive electrode 2 It chooses. If charge and discharge potential furthermore chooses as the material of a solid electrolyte 5 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which shows about 1.55 V, a layered product is formed as a positive electrode 2, a negative electrode 3, and a solid electrolyte 5 combining these, respectively and the charge and discharge potential is measured, it can check that the charge and discharge potential of about 2.2 V is shown.

[0019] As for a solid electrolyte 5, it is optimal that it is the lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) which the lithium oxide containing transition metals, such as Ti, V, Cr, Mn, Fe, Co, and nickel, is used, and the lithium oxide containing transition metals makes a metal lithium a reference potential from the point of latus in selection of such a combination, and has the charge and discharge potential of 1.5–1.6V.

[0020] Thus, if it forms combining the material which shows a solid electrolyte 5, the occlusion of the ion accompanying an electrochemical oxidation–reduction reaction for an electrode 4, and a discharge phenomenon, since the deposit reaction of the lithium accompanying a charge–and–discharge reaction can be suppressed since the metal lithium is not used for a negative electrode and the organic system electrolytic solution will not be used, a liquid spill cannot occur, but safety can be raised.

[0021] While all the above solid-state lithium secondary batteries add and prepare the binder which changes from the organic substance of a Teflon system or a styrene system to solid electrolyte material, a positive electrode 2 and a negative electrode 3 add, prepare and cast the binder which consists of the additive which makes electronic conductivity, such as acetylene black, KETCHIEN black, or a graphite, give active material material, and the organic substance of a Teflon system or a styrene system, and are formed by heat-treating at the temperature of about 80–200 degrees C.

[0022] In all the solid-state lithium secondary batteries of this invention, a solid electrolyte 5 and

the solid polymer electrolyte which contains a solute in an electrode 4 are infiltrated, and a polymerization is carried out. This solid polymer electrolyte consists of any one sort of a polyethylene-oxide system solid polymer electrolyte or the polypropylene oxide system solid polymer electrolyte, or two or more sorts, and a solute is LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiC}(\text{CF}_3\text{SO}_2)_2$. It consists of any one sort or two or more sorts.

[0023] Thus, if a solid electrolyte 5 and the solid polymer electrolyte which contains a solute in an electrode 4 are infiltrated and a polymerization is carried out, while a solid polymer electrolyte can exist in the opening of a solid electrolyte particle or = electrode active material particle, it can make the touch area of a solid electrolyte and an electrode increase and movement of the lithium ion accompanying a charge-and-discharge reaction will become smooth, the internal resistance of a rechargeable battery can be reduced and it can consider as all the solid-state lithium secondary batteries that are excellent in a rechargeable battery property, especially a cycle property.

[0024] As a solid polymer electrolyte, it is desirable to use any one sort of a polyethylene-oxide system solid polymer electrolyte or the polypropylene oxide system solid polymer electrolyte or two or more sorts. Although there are solid polymer electrolytes, such as a polyethyleneimine system, a polyalkylene sulfide system, and a polyvinyl-pyrrolidone system, besides a polyethylene-oxide system solid polymer electrolyte or a polypropylene oxide system solid polymer electrolyte, the polyethylene-oxide system or the polypropylene oxide system solid polymer electrolyte is chemically stable at a charge-and-discharge home, and has the feature from which a deposit of a lithium ion cannot take place easily.

[0025] As a solute, they are LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiC}(\text{CF}_3\text{SO}_2)_2$. It is desirable to use any one sort or two or more sorts. these — others — LiClO_4 , LiPF_6 , and LiAsF_6 etc. — although it is — LiBF_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiC}(\text{CF}_3\text{SO}_2)_2$ etc. — it is thermally stable in a polyethylene-oxide system solid polymer electrolyte or a polypropylene oxide system solid polymer electrolyte, and withstand-voltage nature is high

[0026] A polyethylene-oxide system solid polymer electrolyte or a polypropylene oxide system solid polymer electrolyte can add polymerization initiators, such as a peroxide system or an azo system, to the solid polymer electrolyte in which the solute was dissolved previously, and they can be made it to carry out a polymerization promptly by optical irradiation or heating.

[0027] In addition, as a charge collector 6, metallic foils, such as aluminum (aluminum), copper (Cu), or nickel (nickel), can be used.

[0028] Moreover, if airtightness can be held, there is no limitation of the quality of the material in a package 7, for example, it can use a metal or shrink cases, such as lamination material made from aluminum, nickel (nickel), and aluminum (aluminum), etc. for it.

[0029]

[Example] Next, below, as all the solid-state lithium secondary batteries of this invention were explained in full detail below, they were evaluated.

[0030] (Example) It is LiCoO_2 first as an active material material which constitutes a positive electrode. After mixing [acetylene black] 9 % of the weight for 11 % of the weight and a Teflon system binder as an additive which makes electronic conductivity give to 80% of the weight, addition mixture of the organic solvent well-known into this mixture was carried out by the same weight ratio, and the paste for positive-electrode formation was prepared.

[0031] After mixing [acetylene black] 9 % of the weight for 11 % of the weight and a Teflon system binder as an additive which makes electronic conductivity give $\text{Li}_4\text{Mn}_5\text{O}_{12}$ to 80% of the weight as an active material material which constitutes a negative electrode on the other hand, addition mixture of the organic solvent well-known into this mixture was carried out by the same weight ratio, and the paste for negative-electrode formation was prepared.

[0032] Subsequently, after having applied the object for positive-electrode formation, and the paste for negative-electrode formation on this aluminum foil, respectively, making it fully dry, using an aluminum foil with a thickness of 20 micrometers as a collecting electrode plate and removing a solvent, it adjusted so that the thickness of 80 micrometers and a negative electrode might be set to 75 micrometers in the thickness of a positive electrode by roll pressurization.

[0033] On the other hand, after mixing [$\text{Li}_4\text{Ti}_5\text{O}_{12}$] 10 % of the weight for a Teflon system

binder to 90% of the weight as a solid electrolyte, addition mixture of the organic solvent well-known into this mixture at the same weight ratio was carried out, and the paste for solid electrolyte formation was prepared.

[0034] Next, after having applied the obtained paste for solid electrolyte formation to the positive electrode or the negative electrode, fully drying it and removing a solvent, roll pressurization adjusted the thickness of a solid electrolyte to 20 micrometers.

[0035] therefore — this example — a metal lithium — a reference potential — carrying out — charge and discharge potential — about 4 — V and highest LiCoO₂ the active material of a positive electrode — carrying out — about 3 — Li₄ Mn 5O₁₂ which has the charge and discharge potential of V — the active material of a negative electrode — carrying out — charge and discharge potential — about 1.55 — an electrochemistry element is most constituted with V by making low Li₄ Ti 5O₁₂ into a solid electrolyte

[0036] Moreover, the solid polymer electrolyte which makes the above-mentioned layered product carry out sinking-in hardening is LiBF₄ which serves as a solute in the polyethylene oxide which exists in the shape of a monomer at 92% of the weight. It dissolved 8% of the weight. LiBF₄ After making it dissolve in a N-methyl-2-pyrrolidone in advance, it was made to mix with a monomer-like polyethylene oxide, since it is hard to dissolve in a polyethylene oxide directly. After infiltrating this mixture into the above-mentioned layered product and carrying out evaporation dryness of the NMP at predetermined temperature, the solid polymer electrolyte was infiltrated and the polymerization was carried out. It finished setting up the obtained layered product in the airtight cell for measurement.

[0037] At the temperature of 120 degrees C, after starting the electrode which put the electrode and solid electrolyte layer which were obtained in this way in the size of 30mm angle, since a vacuum drying was carried out, two electrodes were stuck, the layered product was produced, roll pressurization was carried out further, and adhesion was raised for 2 hours.

[0038] (Example of comparison) It is LiCoO₂ as an active material material which constitutes a positive electrode. Except having adopted Li₄ Mn 5O₁₂ as an active material material which constitutes a negative electrode While adjusting the positive electrode to 80 micrometers in thickness like the example 1 so that it might become 75 micrometers in thickness about a negative electrode, it adjusted to 20 micrometers in thickness like the example 1 except using Li₄ Mn 5O₁₂ as a solid electrolyte.

[0039] Moreover, in this example of comparison, sinking-in hardening of a solid polymer electrolyte is not performed to the above-mentioned layered product. After starting the electrode which put the electrode and solid electrolyte layer which were obtained like the example 1 in the size of 30mm angle, Since the vacuum drying was carried out at the temperature of 120 degrees C for 2 hours, the lamination layered product was produced, roll pressurization of the two electrodes was carried out further, and adhesion was raised, and it finished setting up the obtained layered product in the airtight cell for measurement.

[0040] The cell for evaluation obtained in this way is used. (Evaluation) With a charging and discharging device It charges to 2.5V with the current of 500microA as charge conditions at the cell for the aforementioned evaluation. After reaching 2.5V, voltage suspends charge, holds for 5 minutes, and discharges by the discharge current of 500microA to the voltage of after that 0.5V. Next, it charged to 2.0V again, the charge-and-discharge cycle examination which suspends charge and is held for 5 minutes was performed after reaching this voltage, and the cell performance as a rechargeable battery was evaluated in quest of electric discharge quantity of electricity for every fixed cycle.

[0041] Consequently, by the sample of the above-mentioned example of comparison, it turns out to electric discharge quantity of electricity having become 80% or less of initial value in 20 times of charge-and-discharge cycles that electric discharge quantity of electricity holds 80% or more of initial value in the same charge-and-discharge cycle, and it excels in the cycle property by the sample of the above-mentioned example. That is, by infiltrating a solid polymer electrolyte into the opening which exists in a solid electrolyte and an electrode, and carrying out a polymerization to it shows that could make the touch area of a solid electrolyte and an electrode increase, and movement of the lithium ion accompanying a charge-and-discharge reaction

became smooth.

[0042] In addition, this invention is not limited to what was shown in the above-mentioned operation gestalt, in the range which does not deviate from the summary, is changed suitably and can be carried out.

[0043]

[Effect of the Invention] As mentioned above, all the solid-state lithium secondary batteries of this invention Since the solid electrolyte and the solid polymer electrolyte which contains a solute in an electrode were infiltrated and the polymerization was carried out, while the organic system electrolytic solution becomes unnecessary, and a liquid spill does not occur but safety improves Since a solid polymer electrolyte exists in the opening of a solid electrolyte particle or an electrode active material particle, while it can increase the touch area of a solid electrolyte and an electrode and movement of the lithium ion accompanying a charge-and-discharge reaction becomes smooth The internal resistance of a rechargeable battery can be reduced and it can consider as all the solid-state lithium secondary batteries that are excellent in a rechargeable battery property, especially a cycle property.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the cross section showing 1 operation gestalt of all the solid-state lithium secondary batteries concerning this invention.

[Description of Notations]

1 [... A negative electrode, 4 / ... The electrode of a couple 5 / ... Solid electrolyte] All solid-state lithium secondary batteries, 2 ... A positive electrode, 3

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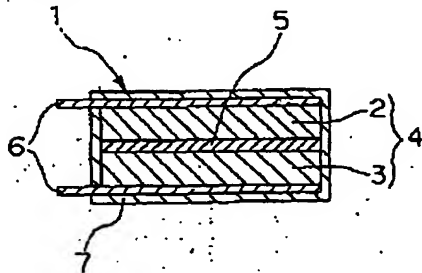
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DRAWINGS

[Drawing 1]



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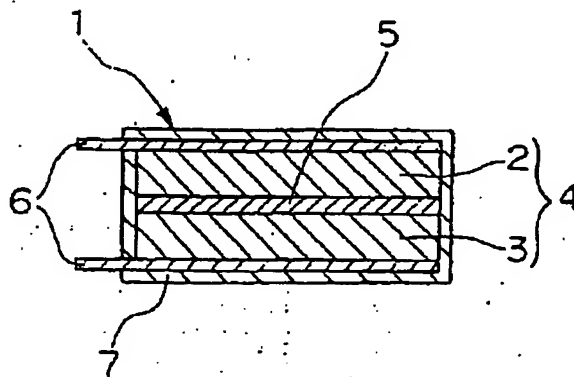
AM16 CJ11 CJ23 DJ09 HJ02

(54)【発明の名称】 全固体リチウム二次電池

(57)【要約】

【課題】 ガスの発生による破裂や電解質の液漏れなどがなく、安全性に優れた全固体リチウム二次電池を提供する。

【解決手段】 固体電解質 5 と電極 4 を電気化学的な酸化還元反応に伴うイオンの吸蔵と放出現象を示す材料を組み合わせ形成した全固体リチウム二次電池において、前記固体電解質 5 および電極 4 に溶質を含む高分子固体電解質を含浸させて重合させた。



【特許請求の範囲】

【請求項1】 固体電解質と電極を電気化学的な酸化還元反応に伴うイオンの吸蔵と放出現象を示す材料を組み合わせて形成した全固体リチウム二次電池において、前記固体電解質と電極に溶質を含む高分子固体電解質を含浸させて重合させたことを特徴とする全固体リチウム二次電池。

【請求項2】 前記高分子固体電解質がポリエチレンオキサライド系高分子固体電解質またはポリプロピレンオキサライド系高分子固体電解質のいずれか一種または複数種から成り、かつ前記溶質が LiBF_4 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 、 $\text{LiC}(\text{CF}_3\text{SO}_2)_2$ のうちのいずれか一種または複数種から成ることを特徴とする請求項1に記載の全固体リチウム二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、電解質として固体状の電解質を用いた全固体リチウム二次電池に関する。

【0002】

【従来の技術および発明が解決しようとする課題】 従来から、正負一對の電極間に水系あるいは非水系の電解質を用いた各種電池が開発されているが、近年のビデオ撮影装置、ノートパソコン、あるいは携帯電話のような携帯用情報端末機器の薄型かつ軽量小型化に伴い、充放電におけるレート特性、サイクル特性、保存特性、あるいはエネルギー密度などの点で満足すべきものではなかった。

【0003】 このような諸特性を満足する電池として、高電圧で高いエネルギー密度を有する二次電池の研究開発が盛んに行われており、特に軽量で再使用可能な小型の二次電池としては、負極に金属リチウムを用いたリチウム二次電池が携帯用情報端末機器の電源用として脚光を浴びている。

【0004】 しかしながら、従来のリチウム二次電池は負極に金属リチウムを用いており、この金属リチウムは反応性に富むものの、燃え易い材料で突然発火する恐れがあることから、安全確保の点で本質的な問題があった。

【0005】 このような問題を解決するために、電極を構成する材料として負極を黒鉛などの層状構造を有する材料に置き換えたリチウム二次電池が提案されている（特開平7-12226号公報参照）。

【0006】 ところが、このリチウム二次電池は層状構造を有する黒鉛などを負極としているため、この黒鉛表面に結合したキノン基やケトン基などの種々の末端基は電気化学的に還元され易いものが多く、1回目の初期充電反応において末端基と電解質が関係した電気化学的還元反応によりガスが発生して電池の内圧が上昇し、電池が破裂したり、電池性能の劣化が生じる他、電解質にリチウム塩を溶解した可燃性の有機系電解液を用いている

ことから、液漏れの問題があり、やはり安全性確保のために、二重三重の安全策が必要であるという問題があった。

【0007】 また、一對の正負極間に有機高分子と有機系電解液からなる固体電解質を介在させて、電解質の流動性を押さえたリチウム二次電池も提案されている（特開平8-315855）。

【0008】 しかしながら、このリチウム二次電池は有機系電解液を含有しており、高温時の充放電過程において、この有機系電解液が分解反応を起こしてガスを発生し、電池の内圧が上昇するという問題がある。

【0009】

【発明の目的】 本発明は、このような従来技術の課題に鑑みて成されたものであり、電解質が酸化還元反応でガスを発生して破裂したり、電解質の液漏れなどが発生することを解消し、安全性に優れ、且つ充放電のサイクル特性が向上した全固体リチウム二次電池を提供することを目的とする。

【0010】

【課題を解決するための手段】 上記目的を達成するために、本発明に係る全固体リチウム二次電池によれば、固体電解質と電極を電気化学的な酸化還元反応に伴うイオンの吸蔵と放出現象を示す材料を組み合わせて形成した全固体リチウム二次電池において、前記固体電解質と電極に溶質を含む高分子固体電解質を含浸させて重合させた。

【0011】 また、上記全固体リチウム二次電池においては、前記高分子固体電解質がポリエチレンオキサライド系高分子固体電解質またはポリプロピレンオキサライド系高分子固体電解質のいずれか一種または複数種から成り、かつ前記溶質が LiBF_4 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 、 $\text{LiC}(\text{CF}_3\text{SO}_2)_2$ のうちのいずれか一種または複数種から成ることが望ましい。

【0012】

【作用】 本発明の全固体リチウム二次電池では、その電解質に液体、特に有機系電解液を使用しないことから、電解質の液漏れが無くなり、さらに電解質が水分や空気と反応を起こすことがなく、また固体電解質と電極に溶質を含む高分子固体電解質を含浸させて重合させることから、従来品では点接触に近い状態にある固体電解質粒子と電極活物質粒子の空隙に高分子固体電解質が存在することになり、固体電解質と電極の接触面積を増加させることができ、充放電反応に伴うリチウムイオンの移動がスムーズになり、二次電池特性に優れた全固体リチウム二次電池とすることができる。

【0013】

【発明の実施の形態】 以下、本発明の全固体リチウム二次電池の実施形態を添付図面に基づき詳細に説明する。図1は、本発明の全固体リチウム二次電池の一実施形態を示す断面図である。図1において、1は正極2と負極

3から成る一対の電極4と、固体電解質5とから成る全固体リチウム二次電池であり、一対の電極4を成す正極2と負極3は、集電体6に塗布されて形成されており、一対の電極4の間に固体電解質5を介在させ、気密性を保持できるパッケージ7で外装して構成されている。

【0014】本発明の全固体リチウム二次電池は、電気化学的な酸化還元反応に伴うイオンの吸蔵と放出現象を示し、且つ後述する充放電電位を有する材料の組み合わせで電極4と固体電解質5が構成されるものであり、かかる現象を示し、所定の充放電電位を有するものであれば特に限定するものではない。例えば LiCoO_2 、 LiNiO_2 、 LiCrO_2 、 LiVO_2 、 $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_4$ 、 LiMn_2O_4 、 LiMnO_2 、 $\text{Li}_4\text{Mn}_5\text{O}_{12}$ 、 LiTiO_2 、 LiFeO_2 、 LiRuO_2 、 LiWO_2 、 $\lambda\text{-MnO}_2$ 、 V_2O_5 、 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 、アナターゼ型 TiO_2 、 Nb_2O_5 などの公知の材料を用いることができる。

【0015】二次電池の起電力を考慮すれば、電極4を構成する材料の充放電電位の差が大であることが望ましく、かつ固体電解質5を構成する材料の充放電電位がそれらよりさらに低いことがより好適である。例えば、電極4を構成する活物質は金属リチウムを基準電位として正極2の充放電電位が2.5～4.0Vである材料から成り、負極3の充放電電位が2.0～3.0Vである材料から成り、また固体電解質5は金属リチウムを基準電位としてその充放電電位が1.5～2.9Vである材料から成ることがより望ましいものである。

【0016】金属リチウムを基準電位とし、その充放電電位が最も低い材料を固体電解質5の材料とし、中間の充放電電位を示す材料を負極3を構成する活物質材料に適用し、最も高い充放電電位を示す材料を正極2を構成する活物質材料として組み合わせ、金属リチウムを基準電位として正極2と負極3の充放電電位の差が大きいことが、より高い充放電電位を得ることができ、望ましい組み合わせとなる。つまり、本発明の全固体リチウム二次電池の充放電電位は、他の二次電池と同様に正極2と負極3の充放電電位の差によって決定されるためである。

【0017】具体的には、金属リチウムを基準電位としてその充放電電位が約4Vを示す LiCoO_2 を正極2を構成する活物質材料として選択すると、負極3を構成する活物質材料には充放電電位が約3Vを示す LiMnO_2 を選択することができ、固体電解質5の材料には負極3を構成する活物質材料の充放電電位よりさらに低い充放電電位を有するものであることが必要であることから、例えば約1.55Vの充放電電位を示す $\text{Li}_4\text{Ti}_5\text{O}_{12}$ を用いることが望ましい。かかる組み合わせにより、それぞれ正極2、負極3、固体電解質5として積層体を形成し、その充放電電位を測定すると、約1Vの充放電電位を示すことが確認できる。

【0018】また、負極3に金属酸化物を使用する具体例としては、負極3を構成する活物質材料に金属リチウムを基準電位としてその充放電電位が約1.8Vを示すアナターゼ型 TiO_2 を選択することができ、正極2を構成する活物質材料に充放電電位が約4Vを示す LiMn_2O_4 を選択し、さらに固体電解質5の材料に充放電電位が約1.55Vを示す $\text{Li}_4\text{Ti}_5\text{O}_{12}$ を選択し、これらを組み合わせてそれぞれ正極2、負極3、固体電解質5として積層体を形成し、その充放電電位を測定すると、約2.2Vの充放電電位を示すことが確認できる。

【0019】固体電解質5は、Ti、V、Cr、Mn、Fe、Co、Niなどの遷移金属を含むリチウム酸化物が用いられ、このような組み合わせの選択が広いという点から、遷移金属を含むリチウム酸化物が金属リチウムを基準電位として1.5～1.6Vの充放電電位を有するチタン酸リチウム($\text{Li}_4\text{Ti}_5\text{O}_{12}$)であることが最適である。

【0020】このように、固体電解質5と電極4を電気化学的な酸化還元反応に伴うイオンの吸蔵と放出現象を示す材料を組み合わせると、負極に金属リチウムを用いていないことから、充放電反応に伴うリチウムの析出反応を抑制でき、且つ有機系電解液を用いないことから液漏れが発生せず、安全性を向上させることができる。

【0021】上記のような全固体リチウム二次電池は、固体電解質材料にテフロン系やスチレン系の有機物から成るバインダーを添加して調製すると共に、正極2と負極3は活物質材料にアセチレンブラック、ケッチェンブラックあるいは黒鉛などの電子電導性を付与させる添加物と、テフロン系やスチレン系の有機物から成るバインダーを添加して調製して成型し、80～200℃程度の温度で加熱処理することにより形成される。

【0022】本発明の全固体リチウム二次電池では、固体電解質5と電極4に溶質を含む高分子固体電解質を含浸させて重合させる。この高分子固体電解質は、ポリエチレンオキシド系高分子固体電解質またはポリプロピレンオキシド系高分子固体電解質のいずれか一種または複数種から成り、かつ溶質は LiBF_4 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 、 $\text{LiC}(\text{CF}_3\text{SO}_2)_2$ のうちのいずれか一種または複数種から成る。

【0023】このように、固体電解質5と電極4に溶質を含む高分子固体電解質を含浸させて重合させると、固体電解質粒子や電極活物質粒子の空隙に高分子固体電解質が存在することになり、固体電解質と電極の接触面積を増加させることができ、充放電反応に伴うリチウムイオンの移動がスムーズになるとともに、二次電池の内部抵抗を低減させることができ、二次電池特性、特にサイクル特性に優れる全固体リチウム二次電池とすることができる。

【0024】高分子固体電解質としては、ポリエチレンオキサイド系高分子固体電解質またはポリプロピレンオキサイド系高分子固体電解質のいずれか一種または複数種を用いることが望ましい。ポリエチレンオキサイド系高分子固体電解質またはポリプロピレンオキサイド系高分子固体電解質以外にも、ポリエチレンイミン系、ポリアルキレンサルファイド系、ポリビニルピロリドン系などの高分子固体電解質があるが、ポリエチレンオキサイド系またはポリプロピレンオキサイド系高分子固体電解質は、充放電家庭で化学的に安定であり、リチウムイオンの析出が起こりにくい特徴がある。

【0025】溶質としては、 LiBF_4 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 、 $\text{LiC}(\text{CF}_3\text{SO}_2)_2$ のうちのいずれか一種または複数種を用いることが望ましい。これらの他にも、 LiClO_4 、 LiPF_6 、 LiAsF_6 などがあるが、 LiBF_4 、 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ 、 $\text{LiC}(\text{CF}_3\text{SO}_2)_2$ などはポリエチレンオキサイド系高分子固体電解質またはポリプロピレンオキサイド系高分子固体電解質中で熱的に安定であり、且つ耐電圧性が高い。

【0026】ポリエチレンオキサイド系高分子固体電解質またはポリプロピレンオキサイド系高分子固体電解質は、先に溶質を溶解させた高分子固体電解質に過酸化化合物もしくはアゾ系などの重合開始剤を添加して、光照射または加熱により速やかに重合させることができる。

【0027】なお、集電体6としては、アルミニウム(A1)、銅(Cu)あるいはニッケル(Ni)などの金属箔を用いることができる。

【0028】また、パッケージ7には、気密性を保持できれば材質の限定はなく、例えばアルミニウム製ラミネート材、ニッケル(Ni)、アルミニウム(A1)などの金属あるいはシュリンクケースなどを用いることができる。

【0029】

【実施例】次に、本発明の全固体リチウム二次電池を以下に詳述するようにして評価した。

【0030】(実施例) 先ず、正極を構成する活物質材料として LiCoO_2 を80重量%に、電子導電性を付与させる添加物としてアセチレンブラックを11重量%、およびテフロン系バインダーを9重量%を混合した後、この混合物に公知の有機溶媒を同一重量比で添加混合して正極形成用ペーストを調製した。

【0031】一方、負極を構成する活物質材料として $\text{LiMn}_5\text{O}_{12}$ を80重量%に、電子導電性を付与させる添加物としてアセチレンブラックを11重量%、およびテフロン系バインダーを9重量%を混合した後、この混合物に公知の有機溶媒を同一重量比で添加混合して負極形成用ペーストを調製した。

【0032】次いで、集電板として厚さ20 μm のアルミニウム箔を用い、このアルミニウム箔上にそれぞれ正

極形成用、負極形成用ペーストを塗布し、十分に乾燥させて溶媒を除去した後、ロール加圧により正極の厚さを80 μm 、負極の厚さを75 μm となるように調整した。

【0033】一方、固体電解質として $\text{Li}_4\text{Ti}_5\text{O}_{12}$ を90重量%に、テフロン系バインダーを10重量%を混合した後、この混合物に同一重量比で公知の有機溶媒を添加混合して固体電解質形成用ペーストを調製した。

【0034】次に、得られた固体電解質形成用ペーストを正極もしくは負極に塗布し、十分に乾燥させて溶媒を除去した後、ロール加圧により固体電解質の厚さを20 μm に調整した。

【0035】したがって、本実施例では、金属リチウムを基準電位として充放電電位が約4Vと最も高い LiCoO_2 を正極の活物質とし、約3Vの充放電電位を有する $\text{LiMn}_5\text{O}_{12}$ を負極の活物質とし、充放電電位が約1.55Vと最も低い $\text{Li}_4\text{Ti}_5\text{O}_{12}$ を固体電解質として電気化学素子を構成したものである。

【0036】また、上記積層体に含浸硬化させる高分子固体電解質は、モノマー状にあるポリエチレンオキサイドを92重量%に、溶質となる LiBF_4 を8重量%溶解した。 LiBF_4 はポリエチレンオキサイドに直接溶解しにくいので、事前にN-メチル-2-ピロリドンに溶解させた後、モノマー状のポリエチレンオキサイドと混合させた。この混合物を上記積層体に含浸させ所定の温度にてNMPを蒸発乾燥させたのち高分子固体電解質を含浸させて重合させた。得られた積層体を測定用の気密セルに組み上げた。

【0037】かくして得られた電極および固体電解質層を被着した電極を30mm角の大きさに切り出した後、120 $^{\circ}\text{C}$ の温度で2時間、真空乾燥させてから、両電極を貼り合わせて積層体を作製し、さらにロール加圧して密着性を向上させた。

【0038】(比較例) 正極を構成する活物質材料として LiCoO_2 を、負極を構成する活物質材料として $\text{LiMn}_5\text{O}_{12}$ を採用した以外は、実施例1と同様にして正極を厚さ80 μm に、負極を厚さ75 μm となるように調整すると共に、固体電解質として $\text{LiMn}_5\text{O}_{12}$ を用いる以外は実施例1と同様にして厚さ20 μm に調整した。

【0039】また、この比較例では上記積層体に高分子固体電解質の含浸硬化は行わず、実施例1と同様にして得られた電極および固体電解質層を被着した電極を30mm角の大きさに切り出した後、120 $^{\circ}\text{C}$ の温度で2時間真空乾燥させてから両電極を貼り合わせ積層体を作製し、さらにロール加圧して密着性を向上させ、得られた積層体を測定用の気密セルに組み上げた。

【0040】(評価) かくして得られた評価用のセルを用いて、充放電装置により、充電条件として500 μA の電流で前記評価用のセルに2.5Vまで充電を行い、

電圧が2.5Vに到達後、充電を停止して5分間保持し、その後0.5Vの電圧まで500 μ Aの放電電流で放電し、次に再度2.0Vまで充電し、この電圧に到達後、充電を停止して5分間保持する充放電サイクル試験を行い、一定サイクル毎に放電電氣量を求めて二次電池としての電池性能の評価を行った。

【0041】その結果、上記比較例の試料では20回の充放電サイクルで放電電氣量が初期値の80%以下になったのに対して、上記実施例の試料では同じ充放電サイクルで放電電氣量が初期値の80%以上を保持しており、サイクル特性に優れていることが分かる。つまり、固体電解質および電極内に存在する空隙に高分子固体電解質を含浸させて重合させることにより、固体電解質と電極の接触面積を増加させることができ、充放電反応に伴うリチウムイオンの移動がスムーズになったことがわかる。

【0042】なお、本発明は、上記実施形態に示したものに限定されるものではなく、その要旨を逸脱しない範囲において適宜変更して実施できるものである。

【0043】

【発明の効果】以上のように、本発明の全固体リチウム二次電池は、固体電解質と電極に溶質を含む高分子固体電解質を含浸させて重合させたことから、有機系電解液が不要となって液漏れが発生せず、安全性が向上すると共に、固体電解質粒子や電極活物質粒子の空隙に高分子固体電解質が存在することから、固体電解質と電極の接触面積を増大させることができ、充放電反応に伴うリチウムイオンの移動がスムーズになると共に、二次電池の内部抵抗を低減させることができ、二次電池特性、特にサイクル特性に優れる全固体リチウム二次電池とすることができる。

【図面の簡単な説明】

【図1】本発明に係る全固体リチウム二次電池の一実施形態を示す断面図である。

【符号の説明】

1……全固体リチウム二次電池、2……正極、3……負極、4……一対の電極、5……固体電解質

【図1】

